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IITRI 1220
(Final Report)

INVESTIGATION RELATING TO THE DEVELOPMENT OF CADMIUM TELLURIDE ENERGY CONVERTERS

National Aeronautics and Space Administration
Headquarters
Office of Propulsion & Power Generation
Code RPP
Washington 25, D. C.
Contract No. NASw - 455

IIT RESEARCH INSTITUTE
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10 West 35th Street
Chicago 16, Illinois

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(Covering the Period from July 10, 1962 to August 31, 1963)

September 30, 1963

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FOREWORD

This is the Final Report on National Aeronautics and Space Administration contract No. NASw - 455, on an "Investigation Relating to the Development of CdTe Energy Converters." It covers the work performed at IITRI during the period from July 10, 1962 to August 31, 1963.

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Data are contained in IITRI Logbooks 12753, 12754, 12755 and 13689.

Respectfully submitted
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ABSTRACT

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This is the Final Report on a project sponsored by the National Aeronautics and Space Administration on "An Investigation Relating to the Development of Cadmium Telluride Energy Converters", under contract No. NASw - 455, covering the period from July 10, 1962 to August 31, 1963. The main findings on this program have been, first the definite need for improved quality single crystal CdTe, second that the production of such material is possible and third a new method of zone refining which is capable of achieving this goal. The first conclusion was anticipated and was confirmed when attempts to make devices from material available initially were found to be irreproducible. The second finding was, in fact, the result of an accident in which some CdTe was cast in the form of a thin, slightly curved layer. It was found to be both single crystal and th have electrical characteristics superior to any material previously reported in the literature. A new vertical zone refining proceedure was developed, as a result of attempts to reproduce this layer, which is better than the previously employed methods in ultimate purity attainable, simplicity and speed. Considerable delay in developing this process was encountered due to persistent devitrification and consequent breakage of the quartz tubes containing the CdTe. This delay resulted in the process not being optimised in the time available before the end of the contract. However vertical zone refining was successfully carried out on several boules.

Auth.

I. INTRODUCTION

This is the final report on N.A.S.A. contract No. NASw-455; covering the period from July 10, 1962 to August 31, 1963, on an Investigation Relating to the Development of Cadmium Telluride Energy Converters. The nature of the program was to investigate the possibility of using cadmium telluride (CdTe) as a photovoltaic solar energy converter. The main objectives of the program were the construction of experimental CdTe single crystal solar cells and the measurement of their properties, both electrical and physical, as a function of illumination intensity, temperature and time.

At the outset, the program was divided into four mutually dependent parts as follows

1. Produce single crystal CdTe suitable for fabricating solar cells.
2. Measure the physical and electrical properties of the material.
3. Fabricate and evaluate experimental cells constructed from the best material produced in 1 as judged by 2.
4. Optimise the crystal growth and fabrication parameters guided by the results of parts 2 and 3.

Of necessity the initial effort was directed towards part 1 above, since some knowledge of junction formation techniques and electrical contacts had been determined previously. It was during this phase of the work that an accident occurred, whilst zone refining was in progress, in which some molten CdTe was spilt out of the boat and became trapped between the boat and the outer quartz containing tube. This material turned out to be single crystal with very good electrical properties. It set a minimum standard to aim for, and by which to judge later material. However, subsequent deliberate attempts to reproduce this crystal by simulating the conditions which occurred during the accident were unsuccessful. Critical reconsideration of the conditions during the accident and those in the simulated experiments suggested a completely new technique for zone refining and single-crystal growing of CdTe. The new method derived involves carrying out the zone refining vertically, instead of horizontally in the manner of Kroger and de Noble[1]. It became apparent that if such a technique was successful it would be a significant advance on the previous technique from a number of viewpoints, not the least of which was the potential ability to produce the purest CdTe available.

Initial experiments with the new method using a temporary furnace and zone refining set-up, indicated that the technique was indeed workable. However some initial difficulties had first to be solved. To this end, a more permanent apparatus was designed and constructed (Fig. 2). Unfortunately, this necessitated delaying the work somewhat. The new furnace came into operation only about 1 1/2 months before the official end of the contract. To date, the technique has been shown to be workable and several zone passes have been made on CdTe boules. It remains only to optimise the furnace conditions for the ultimate potential of the method to be fully realized. The experimental work mentioned briefly above which led to this new process will be described next, followed by a discussion of the results.

II. EXPERIMENTAL WORK AND RESULTS

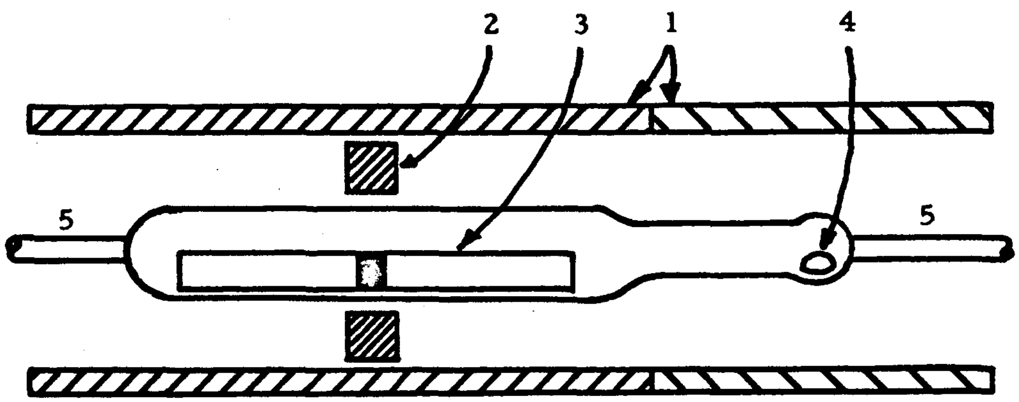
The experimental work has been concentrated chiefly on part one of the four parts into which the program was initially divided. The reasons for this action are presented in the discussion to follow. This section may best be divided into three separate parts:

1. That dealing with the original method of preparation .
2. That describing the accident and subsequent attempts, to simulate the conditions prevailing at the time and subsequently reproduce the cast layer.
3. That dealing with the vertical method of zone refining.

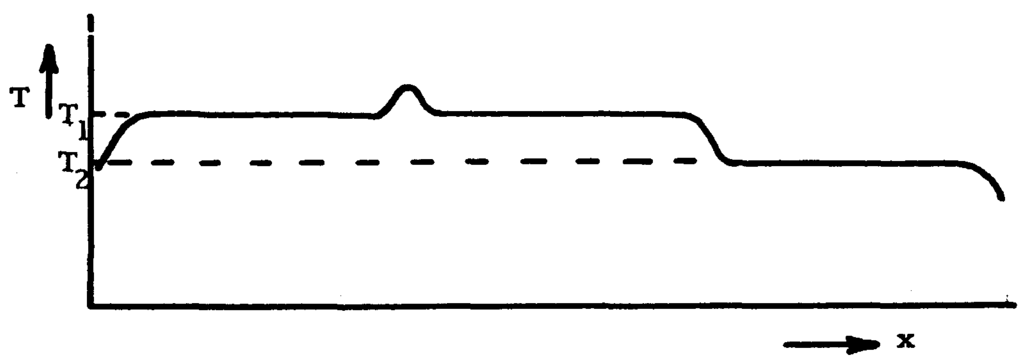
A. Horizontal Zone Refining

The original method of purification attempted here and elsewhere was the horizontal zone refining technique developed by Koger and de Noble[1]. In this process, the cadmium telluride is contained in a quartz boat, carbon coated to prevent sticking, which is in turn contained in an evacuated quartz tube. A smaller quartz tube, containing cadmium metal, is sealed axially to the containing tube and the whole assembly placed in a horizontal zone refining furnace. The furnace is so designed that the ambient temperature above the boat T_1, may be controlled independently of the temperature T_2 in the section containing the cadmium metal (fig. 1). The zone temperature of course must be sufficient to melt the CdTe (mp$\sim$ 1090^{o}C). The reason for this special design is to prevent sublimation of CdTe from the molten zone to colder parts of the tube. By maintaining a constant vapour pressure of cadmium over the boat during zone refining the equilibrium reaction:

1. Double Furnace
2. Zone Heater
3. Boat Containing Cadmium Telluride
4. Cadmium Metal
5. Support Rods



DOUBLE ZONE FURNACE



TEMPERATURE PROFILE

Fig. 1. HORIZONTAL ZONE REFINING APPARATUS

$$2CdTe_{(solid)} \rightleftharpoons 2CdTe_{(vapour)} \rightleftharpoons 2Cd_{(gas)} + Te_{2\,(gas)}$$

is pushed to the left so that essentially no distillation can take place. This relies on the fact that CdTe in the vapour form is almost competely dissociated into cadmium and tellurium, and contributes very little to the vapour pressure itself, as was shown by de Noble[2].

Apart from its complexity, this method suffers from two severe disadvantages. Firstly, it has been shown [2] that only at its maximum melting point do solid and liquid CdTe have the same composition, i.e. stoichiometry. However, due to the excess cadmium vapour pressure, the liquid zone contains excess cadmium. During zone refining, this excess cadmium is segregated at the advancing solid-liquid interface, and, being volatile, causes bubbles to form in the liquid zone. Although these bubbles tend to rise to the surface of the melt, they are easily trapped and built into the solid thereby distorting the lattice and causing the formation of porous, polycrystalline material. To minimize this effect it is necessary to use speeds of zone travel of about 5 mm/hr. These speeds are very restrictive, illustrated by the fact that to pass 12 zones through a boule of 6" length at this speed would require in excess of two weeks even assuming complete automation. The second disadvantage of the de Noble technique is the possibility of distillation of any volatile impurities from the hot zone to colder parts of the boule. This is true of any zone refining method where a surface of the material being processed is exposed for its full length, e.g. floating zone refining. In the latter system however, the walls of the container are the coldest parts and will condense some of the impurities, whereas in the de Noble process the walls of the container are as hot, if not hotter than, the solid parts of the boule. Fortunately, this effect is modified by the presence of the environmental gas through which the impurities have to diffuse.

Despite its shortcomings, this method was the most successful purification technique for CdTe available at the beginning of the program.

B. The Accidentally "Cast" Single Crystal Layer and Attempts at Reproduction

During experiments using the controlled atmosphere furnace for zone refining a polycrystalline boule by the de Noble method, some of the molten CdTe was inadvertantly poured out of the boat and became trapped between the boat and the outer quartz tube. The maintaining temperature at the time was a little higher than usual, approximately 1020°C, and consequently the molten zone was also wider than normal. Two zone passes were made after the accident at a rate of approximately, 0.5 cm/min.

Upon examination afterwards, it was found that although the material in the boat was very porous and polycrystalline, the cast layer was essentially free of bubbles, single crystal and its two slightly curved surfaces were highly polished. If reproducible, this last feature (polished surfaces) would eliminate the difficult and costly task of slicing and polishing a single crystal boule.

Electrical measurements on the cast sample were carried out. It was found to be p-type, with a resistivity ρ, of 3000 ohm-cms. By using a slotted disc mounted on a 10,000 rpm motor to chop a light source, the photoconductive decay was compared with a vacuum photocell and displayed on an oscilloscope. It was found that the decay lifetime of this sample was about 25 micro-seconds. Hall effect measurements were made using a D.C. magnet with 6" pole pieces and a field of 10,000 gauss. The current through the sample was 8.5 microamps. The mean value of the Hall constant (R) from four readings obtained by reversing both the electric and magnetic fields was found to be 35.5×10^{-4} cm^3/coulomb. The mobility, given by:

$$\mu = \frac{8}{3\pi} \quad \frac{R}{\rho} \ cm^2/volt/sec.$$

was calculated to be $102 cm^2$/volt sec., and the carrier concentration $2 \times 10^{-3} cm^{-3}$. The value of the room temperature hole mobility is of particular interest in comparison with those reported by Kroger and de Noble[1] and de Noble[2], namely 35 cm^2/volt-sec and 65 cm^2/volt-sec respectively. This indicated that the material was considerably better than any previously reported and it became a prime aim of the programme to produce material at least as good as the cast crystal.

Three separate experiments were performed in an attempt to simulate the conditions prevailing during the accident. They were designed to produce thin layers of single crystal CdTe of similar quality to the cast layer.

In the first experiment, a quartz tube of 11 mm diameter was flattened on one side to form a D section over about four inches of its length. Small humps were formed in the tube at each end of the flat section to retain the liquid CdTe. Crushed crystals of CdTe were placed in this flat section of the tube, which acted as a boat, and a polished slip of quartz plate, 1/16" thick x 3/8" wide x 4" long was rested on top of the crystals, thus sandwiching them between two quartz surfaces. The tube was then evacuated and sealed as for the de Noble technique. Unfortunately, at the zoning temperatures employed, the flat section of the tube became sufficiently softened to yield under the internal gas pressures. To obviate against this feature, a new tube was constructed using two quartz slips of the same dimensions as before, the first one being sealed into the tube instead of flattening the tube itself. The other rested on top as before.

In both of these experiments severe sticking of the CdTe to the quartz surfaces was encountered, together with the refusal of the material to form a continuous layer due to surface tension forces. Furthermore, those sections of the semi-layer which could be recovered were porous and polycrystalline.

Finally, an attempt was made to zone refine a layer of CdTe contained in a long slot machined in a cylinder of high purity graphite. Some success with this technique was achieved, but true zone refining was not possible since the high heat conductivity of the graphite prevented a narrow liquid zone from being established. This material too was polycrystalline and porous.

Careful reconsideration of all of these experiments, both deliberate and accidental, provided explanations for the results obtained. They pointed up the following significant differences between the original experiment and the attempts at simulation

1. The cast layer was thin. The cast material was trapped between the boat and wall of the tube so that it was squashed into a thin layer. This did not occur in the first two subsequent experiments as the mass of the quartz slip which rested on top of the CdTe was insufficient to overcome the large surface tension forces of liquid CdTe.

2. The cast layer did not stick to the quartz surfaces. It was found that the magnitude of the cadmium vapour pressure during the zone refining or melting of CdTe has a significant effect upon the affinity of the solidified material to stick to quartz surfaces. Such behavior is consistent with the fact that cadmium metal, fused under vacuum in a quartz tube, adheres strongly when it solidifies. This is probably due to the formation of oxides by reaction with the silica or traces of oxygen initially a present as adsorbed or chemisorbed gas, since sticking is prevented if a hydrogen gas environment is employed.

During the deliberate experiments, the cadmium pressure was maintained at about 1.5 atmospheres, whereas, in the casting experiment, particular attention was not paid to the cadmium metal temperatures as zone width was primarily under investigation. It is now known that the cadmium pressure at the time was in fact probably not more than 0.5 atmosphere. Subsequent experiments supported this view.

3. The cast layer was single crystal despite a zone speed of 5 mm per minute.

This is a very interesting and important result. When single crystals are to be grown from the melt by the zone refining technique, it has been found that for best results the zone speeds should be as small as possible, and in practice rarely exceed a few cm per hour. Where this is not the case a polycrystalline boule usually results. However, if the direction of growth is very restricted, as is the case with a layer, higher zone speeds are possible. The reason for this is that only those nuclei initially formed which are favorably oriented, i.e., have their axes oriented such that their maximum growth direction is along the length of the layer, are free to develop, and do so to the exclusion of all the others. This principle is used in all the crystal growth techniques where a seed crystal is not employed. Nevertheless, even with this in mind, single crystal growth at that speed would be rare and appears unlikely, particularly as bubbles were not trapped in the bulk of the material.

What appears to have happened in fact is that, although the zone heater speed was large (i.e., 0.5 cm/min), the rate of crystallization within the layer was controlled more by the presence of the boat and its contents than by the movement of the zone heater. Since the large mass of CdTe melt in the boat would not crystallize at the zone speed, the actual rate of crystallization within the layer would be similarly reduced.

4. The cast layer was free of bubbles. It has already been shown why CdTe zone refined by the de Noble technique has a pronounced tendency to have bubble inclusions (c.f.-p.5) The absence of bubbles in this case may be explained as follows.

Firstly, as mentioned previously, the cadmium pressure was lower than is normally employed so that the composition difference between solid and liquid was less*. Secondly, the width of the layer was at an angle to the horizontal so that the bubbles were free to rise to one side of the layer which was not so in the 'sandwich' type experiments. (Upon examination of the cast it was found that there were some bubbles included along one edge - the upper exposed edge).

Finally, due to the presence of the boat and its melt on one side, the surface of the cast in contact with the boat would have been the last

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* Sublimation would not be serious since only a narrow edge of surface was exposed.

to freeze so that the bubbles could escape during a substantial part of the solidification. Normally they tend to become trapped under the surface of the boule since the surfaces are the first parts to freeze by radiative cooling.

C. The Vertical Zone Refining Method

From these considerations, a new technique emerged which not only simplified the process of zone refining CdTe but also had inherent advantages over the horizontal technique with regard to the ultimate purity obtainable.

Briefly the new technique is to zone refine cadmium telluride vertically in sealed quartz tubes with a minimum unoccuppied volume above the solid and no cadmium back pressure. The advantages which this approach has are enumerated below.

1. The solid and liquid can have the same composition, i.e., stoichiometric. This is because sublimation can only occur at the top surface, which is small, and will in any case be rejected ultimately. As a result bubbling and consequent porosity are suppressed.

2. The transport of volatile impurities to the refined parts of the boule cannot take place since the solid material above and below the molten zone act as seals. Hence ultimate purity should be higher for this technique.

3. By arranging for the zone to move upwards along the containing tube, (or the tube downwards through the hot zone), any bubbles which do form, as a result of slight deviations from stoichiometry or volatile inclusions, will rise away from the solidifying interface to the melting interface and thus considerably reduce the chances of

being trapped in the solid material.

4. Since no cadmium back pressure need be applied, the process is simplified and the number of variable parameters reduced. This has the dual advantage of reducing the cost of the method, and of reducing the number of parameters which must be adjusted in attempting to optimise the resulting material.

5. The Bridgeman-Stockbarger seeding technique can be easily employed by terminating the end of the tube in a point, so that selective nucleation occurs.

6. The zone speeds which may be employed can be increased considerably, and are limited only by the thermal conductivity of the material rather than being restricted by porosity considerations.

Vertical zone refining in sealed tubes is not in itself a new technique and has previously been applied widely to low melting point organic materials, as well as to some semi-conductor compounds by T.C. Harmon et al[(3)], and to bismuth telluride by F.K. Heumann[(4)]. Weisberg and Celmer[(5)] also attempted to use the technique for arsenic purification but found it to be unsuitable due to persistent fracture of the containing tube. However, it has not been previously employed for the purification of CdTe. At IITRI we have succeeded in developing the technique for use with this material. Boules of about 1 cm diam by 10 cm long have been zone refined in a specially built furnace (fig. 2) using zone speeds ranging from 2 cm/hr. to 10 cm/hr. The resulting material was completely free of bubble inclusions and had highly polished surfaces. Sticking of the CdTe to the quartz was prevented by the introduction of a small quantity of hydrogen gas after

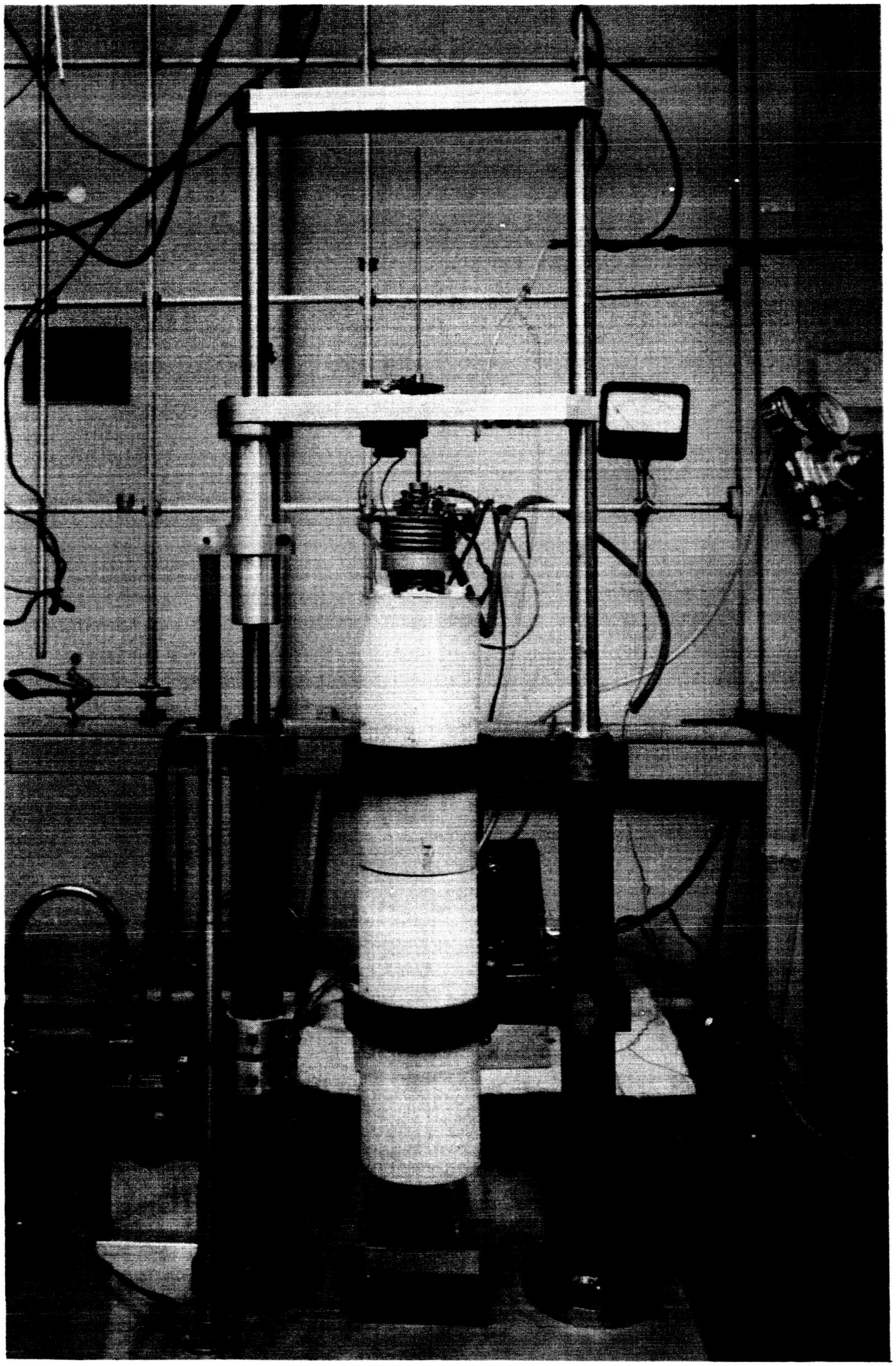

Fig. 2 VERTICAL ZONE REFINING FURNACE

evacuation and prior to sealing. Although the material produced so far has not been completely single crystal, the boules produced did exhibit large single crystal areas, and no particular problems are anticipated in growing them into single crystal form under carefully controlled conditions. Up to this point the emphasis has largely been on establishing the feasibility of the vertical zone refining technique for CdTe.

In view of the fact that single crystals have not been produced so far by this technique, and because the conditions have not yet been optimised, few electrical measurements on this material have been performed. Those measurements that have been made showed the material to be of high resistivity, and n-type.

V. CONCLUSIONS

It has already been pointed out that, even in the initial stages of the program, it was realized that some improvement in the quality of the available CdTe was required for the construction of successful solar cells. Devices constructed initially were irreproducible and, as a result, systematic investigation of the degrading (or beneficial) effects of various fabrication proceedures became virtually impossible. The accidental production of a cast single crystal of superior quality demonstrated both the attainability and potential of really good CdTe. For these reasons, it was considered of great importance to follow up the accident with a deliberate series of experiments designed to determine the causes of the cast layer's high quality. The result of these experiments, a new zone refining technique, we consider to be a real step forward both in the potential ability to produce good material and in the eventual construction of useful solar cells.

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